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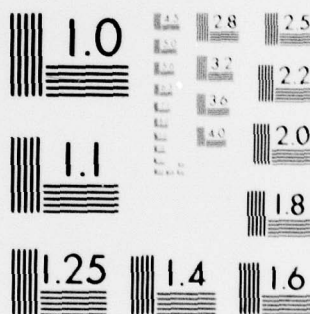
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CALLERY CHEMICAL COMPANY

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THE BALLISTIC MISSILE DEFENSE ADVANCED TECHNOLOGY CENTER
P.O. BOX 1500
HUNTSVILLE, ALABAMA 35807

on

6 CARBORANE SYNTHESIS.

15 DASG-60-78-C-0146

CONTRACT NO. DASG-60-78-C-0146
CALLERY CHEMICAL COMPANY JOB NO. AC-970

AUGUST 28, 1979

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ABSTRACT

✓ This report describes Phase I work done under Contract DASG-78-C-0146 for the scale-up studies in thermolysis of tetraethylammonium borohydride(1-), (Et_4NBH_4) to tetraethylammonium decahydrodecaborate(2-), $[(Et_4N)_2B_{10}H_{10}]$, during the period from October 1978 to June 1979.

→ The objective of this Phase I program was to solve the heat transfer requirements occurring during thermolysis. The nature of this requirement was to identify and optimize the reaction conditions of scale-up using boron and non-boron based solvents in the conversion of Et_4NBH_4 by thermolysis to $(Et_4N)_2B_{10}H_{10}$.

The critical steps in this requirement were to dissipate exothermic heat to minimize $(Et_4N)_2B_{12}H_{12}$ by-product formation and to maximize the desired $(Et_4N)_2B_{10}H_{10}$ product.

Thermolysis of Et_4NBH_4 , using triethylamine borane (Et_3NBH_3) as a boron-based solvent was demonstrated on a 50 g scale with $(Et_4N)_2B_{10}H_{10}$ yields up to 60%.

Thermolysis of Et_4NBH_4 using mineral oil as the non-boron based solvent, demonstrated 47% yields.

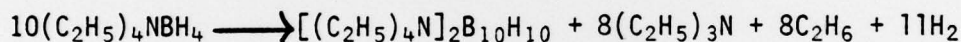
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SUMMARY

The objective of this program was to solve a heat transfer problem involved in the scale-up of one step in the process developed by Auburn University for the synthesis of carboranes before undertaking the batch production of 15 pounds of carboranylmethyl propionate, (CMP). Specifically, the problem involves heat transfer during the thermolysis conversion of Et_4NBH_4 to $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$.

A reaction system was fabricated such that measurements of physical factors and by-products of the reaction could be made to follow the course of the thermolysis reaction:



Evaluation of the heat transfer-solvents Et_3NBH_3 and mineral oil was accomplished by thermalizing 50 g of Et_4NBH_4 in 25 to 200 g of the candidates and comparing $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ yields. Thermolysis was carried out at slightly above one atmosphere in a 3 inch diameter pyrex glass process pipe, one liter and 3 neck 300 ml round bottom stirred reactors heated by an oil bath. Temperature profiles of both the bath and the internal reaction media were measured to gather data useful in determining the course of the thermolysis for engineering evaluations.

Variations in temperature, reaction duration and quantity of heat transfer solvent were studied to optimize the reaction conditions.

Approximate yields of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ were determined by product weight and an estimate of $\text{B}_{10}\text{H}_{10}^{2-}$ vs Et_4N^+ and $\text{B}_{12}\text{H}_{12}^{2-}$ and other impurities by an in-house infrared analysis method. Simultaneously, samples were submitted to Auburn University for liquid chromatograph (L.C.) and the University of Utah for nuclear magnetic resonance (N.M.R.) analyses to cross-check the results.

The first studies in the thermolysis of Et_4NBH_4 to the $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ salt gave intractable mixtures of materials containing large amount of oxyborates due to the fact that our supplier of Et_4NBH_4 provided starting material of less than 80% purity. Consequently, the program was delayed for several months until this vendor was able to supply Et_4NBH_4 of acceptable purity (99%).

Early thermolyses of Et_4NBH_4 were discouraging. The evolution of off gas H_2 and C_2H_6 ceased at 60 to 80% of theory, the triethylamine recovered ranged between 10 and 50% of theory. Product solids recovered containing approximately 50% $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ were 30 to 80% of the expected amounts. Variations in temperature, reaction duration and solvent quantities did not appreciably alter the trend of incomplete reaction. Apparently thermolysis reaction was suppressed at an intermediate stage by the containment of triethylamine in the glass pipe reactor.

A 300 ml glass reactor design was then designed that approximated a single plate distillation system to facilitate triethylamine borane removal, and more complete reaction resulted. Off gas H_2 and C_2H_6 increased to near theoretical and the amine recovered was substantially greater, but still only 70 to 80% of theory. Product solid recovery was 80 to 100% with overall yields of $(Et_4N)_2B_{10}H_{10}$ about 60%.

To define and optimize the thermolysis of Et_4NBH_4 to $(Et_4N)_2B_{10}H_{10}$ the reaction temperature and duration was varied to determine the effect on yield. From the data a trend toward higher overall yield of $(Et_4N)_2B_{10}H_{10}$ was observed when reaction temperatures of 180 to 185°C was rapidly attained with shorter overall reaction times.

When the thermolysis was run at lower temperatures (150-165°C) the total solid product was not only much less than theory, 35%, but the yield of $B_{10}H_{10}^{-2}$ vs $B_{12}H_{12}^{-2}$ favors the B_{12} . Although the $B_{10}H_{10}^{-2}$ is thermally stable at these temperatures, too long a heat soak causes further interreaction with 40-50% yields of $(Et_4N)_2B_{12}H_{12}$.

The higher yields, in Et_3NBH_3 , of $B_{10}H_{10}^{-2}$ over $B_{12}H_{12}^{-2}$ was obtained at 180 to 185°C with minimum reaction times. For instance comparing Runs 23, 25 and 16 at 177°C and 4 hours reaction time the product contains more $B_{10}H_{10}^{-2}$ than at 7-1/2 hours, with 36% and 24% yields respectively.

Heat transfer-solvent Et_3NBH_3 was also varied to find the optimum concentration. A trend toward higher overall yield of $(Et_4N)_2B_{10}H_{10}$ resulted when the concentration of heat transfer solvent Et_3NBH_3 was reduced. With a Et_4NBH_4 to Et_3NBH_3 ratio of 1:3, a yield of 27%, $B_{10}H_{10}^{-2}$ results, compared to 40% with a 1:0.67 concentration.

Mineral oil was evaluated as a non-boron heat transfer solvent in the thermolysis of Et_4NBH_4 . All the favorable process variables developed for Et_3NBH_3 were combined, and mineral oil was substituted for comparison. Although reaction time required for complete reaction was much longer with mineral oil, 8 hours at 183°C, the single run $(Et_4N)_2B_{10}H_{10}$ yield of 47% was encouraging. Further evaluation of mineral oil as a heat transfer-solvent medium is planned in the on-going carborane studies. Mineral oil would be a preferred heat transfer-solvent based on cost, handling and disposal in a scaled process.

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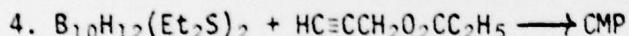
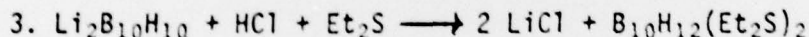
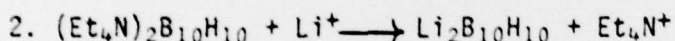
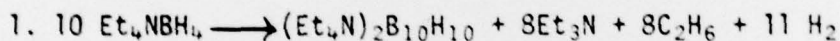
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TECHNICAL BACKGROUND AND PROCESS CONCEPT

A potential technological breakthrough for synthesis of carboranes from a hydroborate(1-), which does not involve diborane(6) or decaborane(14) intermediates, has emanated from the program sponsored by BMDATC at Auburn University (SOW-SW-A-66-76). Dr. W. E. Hill and Dr. F. A. Johnson have demonstrated in the laboratory that Et_4NBH_4 can be converted to $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ in the manner published by Callery Chemical Company in 1967. In the earlier work difficulty was encountered in the conversion of this $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ derivative to a decaborane(12) intermediate precursor to carboranes, and maximum yields were of the order of 30% (1, 2, 3). However Dr. Hill and Dr. Johnson showed that if the tetraethylammonium salt is first converted to the lithium salt by ion exchange, yields of decaborane(12) derivative, $\text{B}_{10}\text{H}_{12}(\text{Et}_2\text{S})_2$, yields can be achieved in excess of 80%.

As a result of these findings simple reaction equations can be written for the production of carboranes from Et_4NBH_4 , which do not involve diborane(6) and decaborane(14) intermediates.



Equation (4), the conversion of $\text{B}_{10}\text{H}_{12}(\text{Et}_2\text{S})_2$ to a carborane, has been demonstrated on a multipound scale.

Scale-up of the reaction of equation (1), thermolysis of Et_4NBH_4 to decahydrodecaborate(2-) had been studied previously with decreasing yields of the decahydrodecaborate(2-). (3) Thus, this work (DASG-60-78-C-0146) was to demonstrate the thermolysis of Et_4NBH_4 to $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ on at least a 50 g scale.

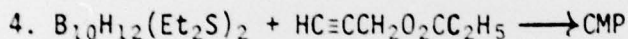
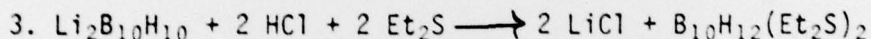
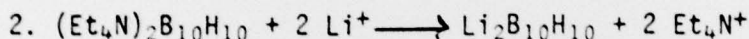
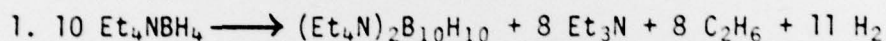
The process concept in the conversion of the Et_4NBH_4 to the $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ derivative was to study the effect of using boron and non-boron based solvents as heat transfer agents to control the reaction temperature.

Solution of the thermolysis problem in the synthesis of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ was done in two stages:

- (1) The conditions of concentration, time and temperature were optimized for conversion of 50 g quantities of Et_4NBH_4 to $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ using a high boiling boron based solvent, triethylamine borane, in varying amounts.
- (2) Using optimum conditions, non-boron solvents compatible with the system were used in place of the borane solvent to determine if comparable yields were obtained. Solvents such as mineral oil, high boiling amines and ethers were to be evaluated.

RESULTS AND DISCUSSIONS

A process has been demonstrated for the production of carboranes from simple hydroborates, by-passing diborane(6) and decaborane(14) intermediates. The process consists of the following reaction sequence, starting with Et_4NBH_4 and going to the desired carborane product, CMP:



The process is made possible by the successful production of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ by the thermolysis of Et_4NBH_4 (step 1) and the conversion of $\text{Li}_2\text{B}_{10}\text{H}_{10}$ to $\text{B}_{10}\text{H}_{12}(\text{Et}_2\text{S})_2$ (step 3). For this first phase of the scale-up feasibility study, only the step 1 thermolysis of Et_4NBH_4 was evaluated.

Preparation of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ - Occurs in excellent yield on a 2 g scale upon heating Et_4NBH_4 , as dry powder, to temperatures of 185-190°C. Ideally the reaction is as step 1 above illustrates. In the dry process, the reactants pass through a phase change when heated to 185-190°C. During heat up, at a temperature of around 120°C, the solid starting material melts to a bubbling opaque mass, then quickly resolidifies. Gas evolution starts below 100°C and continues throughout the thermolysis. Yields of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ were of the order of 80% on a 2 g scale in the 1966-67 work (3). Recent thermolysis under autogenous pressure has produced up to 97% yields of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$, on a 5 g scale (4).

The earlier scale-up with increasingly larger dry powder charges of Et_4NBH_4 gave increasingly higher yields of dodecahydrododecaborate(2-). The product distribution was obtained from infrared and N.M.R. analyses. The failure to dissipate exothermic heat during thermolysis on the larger scale was suspected of causing the production of the $(\text{Et}_4\text{N})_2\text{B}_{12}\text{H}_{12}$ by-product.

Solution Thermolysis of Et_4NBH_4 was proposed to solve the heat transfer problem in the synthesis of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$. Interreaction of Et_4NBH_4 and triethylamine borane did not occur at temperatures up to 170°C in earlier studies (3). Therefore, the excellent solvent and high boiling properties of triethylamine borane recommended it as the boron-based solvent to be evaluated. Optimized yields of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ in the 60% range were obtained when Et_4NBH_4 thermolysis was carried out in triethylamine borane.

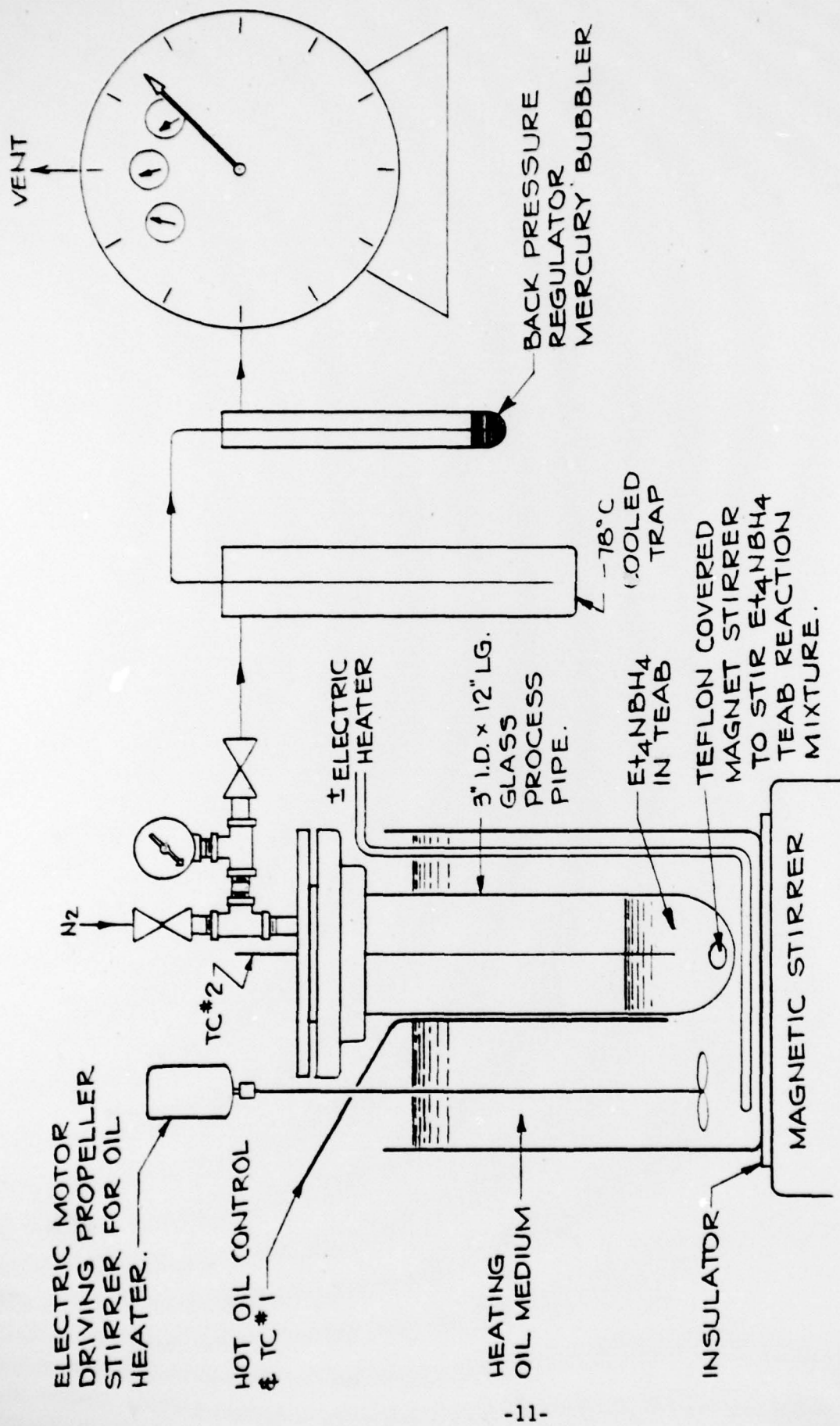
Mineral oil was selected as the non-boron solvent of first choice for heat transfer during thermolysis. Economics and intermediate solubilities recommended mineral oil. A yield of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ in the 33 to 47% range was demonstrated by substituting mineral oil in the above triethylamine borane optimized process.

Thermolysis of Et_4NBH_4 in Et_3NBH_3 Solvent - Reactions were run at slightly above one atmosphere in a pyrex reaction kettle. Figure I illustrates the basic reactor design.

The one liter, glass pipe reactor was stirred by a teflon covered magnet. Temperatures were constantly monitored in the center of the reactor in the liquor, just above the stirrer and outside the reactor in the oil bath. Heat was supplied by electric immersion heater. Reactor pressure, 0.8 to 1.2 PSI, was maintained by a back pressure regulator, consisting of an appropriate sized mercury bubbler.

By-product triethylamine was condensed out of the off-gas stream in a -78°C cooled cold trap. Triethylamine borane was found in the condensate also, as much as 50%. The non-condensed ethane and hydrogen were measured by a wet-test gas meter to follow the rate of reactions. When the reaction was terminated, the product-solution was quickly cooled to room temperature by removing the hot oil bath.

Recovery of the thermolysis products by filtration was facilitated by their insolubility in the triethylamine borane heat transfer solvent. N.M.R. spectra confirmed their complete insolubility. The resulting filter cake, containing the $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$, was washed three times with hexane to remove residual triethylamine borane. Following drying, approximate yields were determined by product weight and estimates of $\text{B}_{10}\text{H}_{10}^{(2-)}$ and by-products by in-house infrared analyses. Simultaneously, samples of the products were submitted to Auburn University to confirm these results by Nuclear Magnetic Resonance (N.M.R.) and a liquid chromatograph method developed by Dr. W. E. Hill et al. Additional confirmation of the product was obtained by submitting samples to Drs. R. W. Parry and G. Kodama of the University of Utah, for nuclear magnetic resonance analysis. Figure II shows a typical N.M.R. spectra of the thermolysis product, obtained from the University of Utah.



THE TC#1 & 2 COUPLES ARE SET
UP ON A 24 POINT RECORDER

FIGURE 1
1 LITER THERMOLYSIS REACTOR

The top spectrum in Figure II shows H-B coupling while the bottom spectrum shows the proton decoupled spectrum. Interpretation of the data on spectra relative to BF_3 standard was made by Dr. Parry. Relative yields of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ and by-products was obtained by calculating the area ratios under each assigned compound. Detrimental nuclear Overhauser effects were reportedly kept at a minimum by system decoupling at the appropriate proton field strength. These results are in general agreement with Auburn University N.M.R. and liquid chromatographic results. Any differences in results were most likely due to solution problems in introducing the thermolysis product to the respective analytical instrument.

The initial scale-up investigated the variables temperature, reaction duration and triethylamine borane concentration to minimize $\text{B}_{12}\text{H}_{12}^{2-}$ formation and maximize $\text{B}_{10}\text{H}_{10}^{2-}$ yield. Thermolysis results are described in Table I, in terms of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ yield and boron distribution ratio of the various compounds synthesized. N.M.R. provided the basis for identifying the compounds produced. Process development relied on in-house infrared analyses to determine comparative $\text{B}_{10}\text{H}_{10}^{2-}$ yields for near-term evaluation.

Run data has been omitted from Table I for the first six runs. These first scale-up thermolyses of Et_4NBH_4 gave intractable mixtures of materials, largely contaminated with hydroxy borates, due to below specification grade Et_4NBH_4 from the supplier. Run 7 utilized an in-house purified Et_4NBH_4 , while those following used specified purity 99 plus % starting material.

The recommended reaction temperature of 185°C was evaluated by maintaining the heating oil bath at that temperature in Runs 7, 9, 12 and 13. As can be seen in Table I, the internal reaction temperature was 3, 8, 12 and 17°C lower. The same effects were noted in runs of 167° and 195°C .

Several trends were observed in the results from these 6 runs. The evolution of gas, non-condensed H_2 and C_2H_6 , ceased at 60 to 85% of theory, and the triethylamine by-product recovered was only a fraction of theory. The solids recovered, containing the $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$, were only 30 to 80% of the amount expected.

Run 13 showed the most promise with a 50% yield based on N.M.R. and a 37% yield based on L.C. and gross product weight.

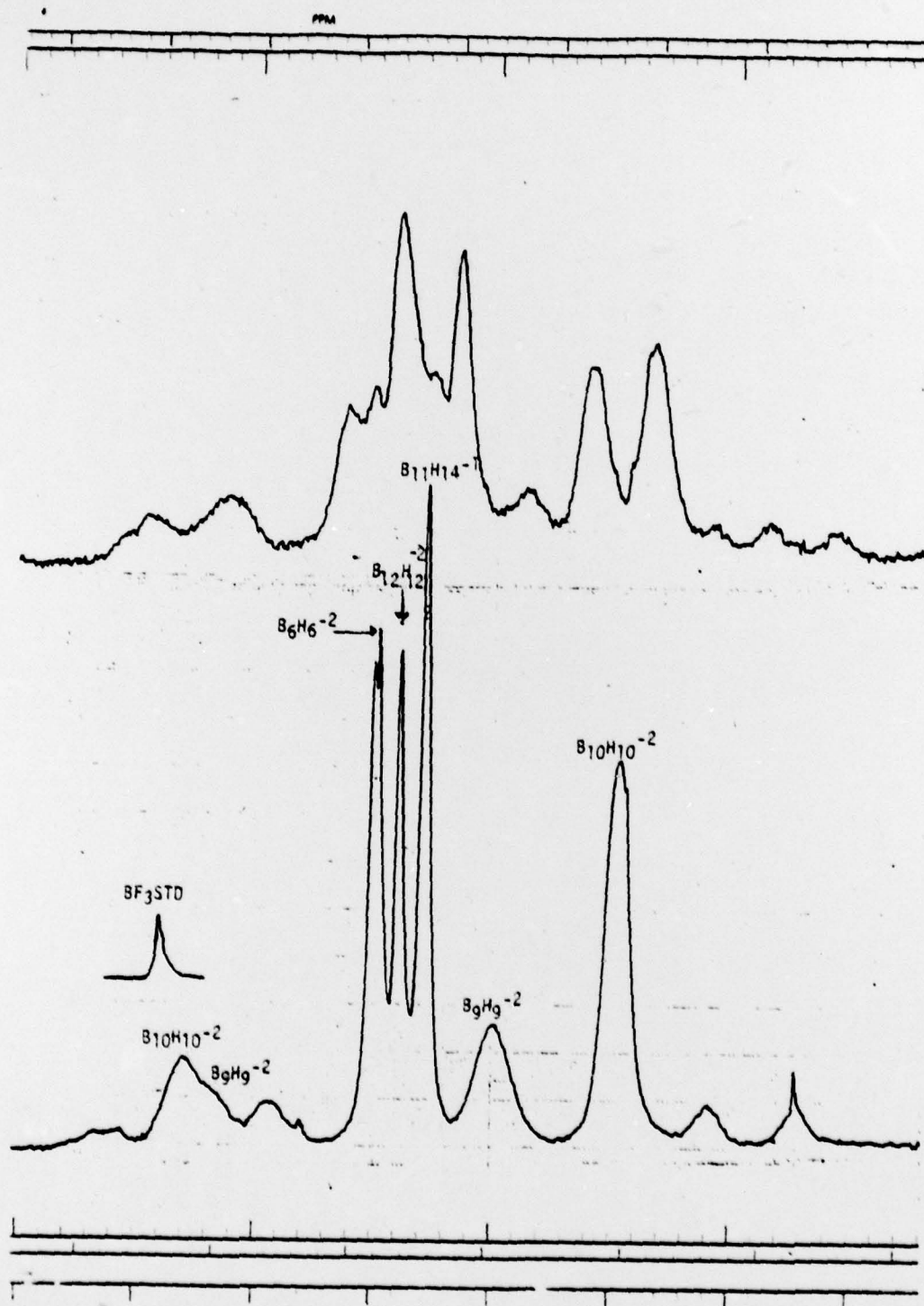


FIGURE II
B" NMR OF THERMOLYSIS PRODUCT

TABLE I
THERMOLYSIS SUMMARY

RUN #	QEMA, MOLES	TEAB MOLES	TEMPERATURE OIL C Rx C	TIME HRS	OFF GAS L	TEAB REL. MOLES	TEA REL. %	PRODUCT G	M. R. UNIVERSITY UTAH				YIELD $B_{10}H_{10}$ VIA N.M.R. %	INFRARED DISTRIBUTION %		L.C. AND N.M.R. AUBURN UNIVERSITY YIELD BASED ON L.C. %				
									BOWEN DISTRIBUTION					YIELD $B_{10}H_{10}$ VIA N.M.R. %	$B_{10}H_{10}^{-2}$ %	$B_{12}H_{12}^{-2}$ %	$B_{10}H_{10}^{-2}$ %	$B_{12}H_{12}^{-2}$ %	$B_{10}H_{10}^{-2}$ %	$B_{12}H_{12}^{-2}$ %
									$B_{10}H_{10}^{-2}$ %	$B_{12}H_{12}^{-2}$ %	$B_{11}H_{11}^{-1}$ %	$B_8H_8^{-2}$ %								
7	0.289	1.76	182	179	8.2	66	1.82	29	6.0	55	31	16.2	6.5	3.9	21	100	16.1	10	2.8	4.6
9	0.354	0.87	182	174	11.7	77	.88	32	8.0	60	37.6	16.7	16.7	17.6	27	70	20.7	30	12.7	18.4
10	0.345	0.87	167	161	9.0	61	1.07	10	4.0	31	42.1	3.1	24.5	3.4	13		20.2	27	6.2	8.3
11	0.345	0.87	195	182	12.0	81	1.02	12	9.4	72	55.2	12.1	17.0	15.7	28	78	34.1	40	14.1	16.5
12	0.345	0.43	185	173	11.5	79	0.43	50	8.0	61	15.2	75.3		2.3	12	67	24.0	10	11.0	4.6
13	0.345	0.22	185	168	12.5	85	0.18	47	10.5	81	55.9	7.2	10.6	4.0	50	75	51.2	65	36.8	46.8

Consideration of the refluxing liquid observed in the reactor with a 137 to 145°C temperature profile suggested that the refluxing liquid in the ullage was other than triethylamine, which boils at 89.5°C. The amine recovered in the cold trap contained as much as 50% triethylamine borane. Since the triethylamine borane has a boiling point over 200°C, the formation of a triethylamine-triethylamine borane constant boiling mixture was suspected of preventing the theoretical amount of the triethylamine from escaping the reactor in the off gas stream.

Therefore the constant return of triethylamine to the reaction liquor might suppress the thermolysis reaction at some intermediate stage. Equilibrium shift and reaction completion were assumed to be possible by removing the byproduct triethylamine from the reactor.

Thus a reactor was designed to facilitate amine removal as shown in Figure III.

The reactor, illustrated in Figure III, considered of a 300 ml, 3 neck round bottom flask. Stirring was provided by a teflon covered magnet. An immersion thermometer measured the temperature of the reactor liquor. Heating was provided by total immersion in an oil bath, which was electrically heated and stirred. Off gas left the reactor through a connection lagged with electric heating tape to reduce reflux, to an air cooled cross-over and finally to a room temperature receiver. Following were a 0°F and -78°C cooled vapor traps then the wet test gas meter to measure noncondensed H₂ and C₂H₆.

Resizing and redesigning the reactor for thermolysis of 50 g charges of Et₄NBH₄ changed the reaction characteristics. Off gas and triethylamine by-products released were near theoretical values, as Table II illustrates.

Heating bath and internal reaction temperatures were notably similar due probably to the lack of cooler reflux liquid returning to the area.

Runs 16 through 20 evaluated reaction temperature as the controlling variable to increased (Et₄N)₂B₁₀H₁₀ yields. Temperatures below 177°C did not increase the yield, nor did stepwise increases as in Run 20.

Run 21 repeated Run 13 reactor temperature and triethylamine borane content conditions. Apparently Run 13 reaction temperature was somewhat above the recorded temperature because Run 21 never attained similar off gas or solid product proportions.

TABLE II
THERMOLYSIS SUMMARY

RUN #	Q _{BNH₄} MOLES	TEAB MOLES	TEMPERATURE OIL °C	TEMPERATURE RX °C	TIME HRS	OFF GAS L %	TEAB REL. MOLES	TEA REL. %	PRODUCT G %	N.M.R. UNIVERSITY UTAH				YIELD B ₁₀ H ₁₀ VIA N.M.R. %		INFRARED DISTRIBUTION B ₁₀ H ₁₀ %		L.C. AND N.M.R. ALUMIN UNIVERSITY			
										B ₁₀ H ₁₀ %	B ₁₀ H ₁₂ %	B ₁₀ H ₁₄ %	B ₁₀ H ₁₆ %	B ₁₀ H ₁₀ %	B ₁₀ H ₁₂ %	B ₁₀ H ₁₄ %	B ₁₀ H ₁₆ %	B ₁₀ H ₁₀ %	B ₁₀ H ₁₂ %	B ₁₀ H ₁₄ %	B ₁₀ H ₁₆ %
16	0.345	0.87	177	177	7.5	14.4	98	0.62	78	12.5	96	24.8	43.9	17.1	6.5	7.6	24	24.9	35	23.8	34.4
17	0.345	0.87	166	166	7.5	13.3	91	0.78	70	11.0	84	29.7	38.5	13.3	3.1	15.3	25	22.6	35	19.0	29.4
19	0.345	0.91	156	156	25	10.5	72	0.95	40	4.8	37	Not analysed insufficient product						18.8	25	6.9	9.2
20	0.345	0.87	130 to 180		46	31	210	unknowns	1.8	Not analysed insufficient product								Insufficient product			
21	0.345	0.22	169	168	24	13.2	90	0.17	67	8.5	65	Not analysed insufficient product						30.7	40	25.2	26.0
22	0.345	0.87	211-200		35 min	10.6	72	-----	4	31		Not analysed insufficient product						Insufficient product			
23	0.345	0.43	177	176	4	14.8	101	.27	--	11.4	97	44.5	15.8	24.8	15.1			36.1	40	36.1	36
24	0.345	0.47	177	177	1	15.3	104	.27	--	12.6		40.4	17.5	21.8	12.4			54.0	55	52	52
25	0.345	1.3	177	177	4	14.5	99	1.09	82	11.6	89	39.5	18.4	22.4	12.5			26.9	25	20	23.8
26	0.345	1.3	127	125	0.5	0.43															
			167	165	2	8.5															
			177	173	0.5	10.4															
			187	184	2	13.7															
			192	188	2	15.6	106	1.18	--	8.2	63	---	58.2	21.2	20.6			3.5	5	2.2	3.0
27	0.345	0.87	175	175	1	8.4															
			186	182	2	14.8	101	0.63	--	13.0	100	25.9	22.1	23.2	14.3	14.5		26.4	25	26.2	24.9
28	0.345	1.087	186	183	1.5	16.7	114	0.74	114	15.0	115	24.0	37.4	25.2	7.9	5.5		23.2	35	26.6	40.2
29	0.345	0.6	186	183	1.5	15.0	102	0.53	--	13.5	104	31.1	10.9	26.1	20.6	11.2		39.9	35	41.2	36.2
30	0.345	0.609	186	181	1.5	15.2	103	0.49	--	13.2	101							44	40	44.5	40.4
31	0.345	0.217	186	181	2.5	13.6	92	0.16	81.5	14.0	108	59.9	11.4	8.4	11.2	8.1		37.5	65	40.2	69.7
33	0.345	0.043	186	180	3.5	13.2	90	--	81.7	14.3	--	Excessive BH ₄ remains						--	--	--	--
34	0.345	0.233	187	181	2.5	15.6	106	0.17	--	13.7	105	46.5	9.9	9.6	15.5	10.6		34.6	53	36.3	55.6
35	0.345	25.9 M.O.	187	183	8.0	13.5	92	--	66	10.3	79							42.5	60	33.5	47.3

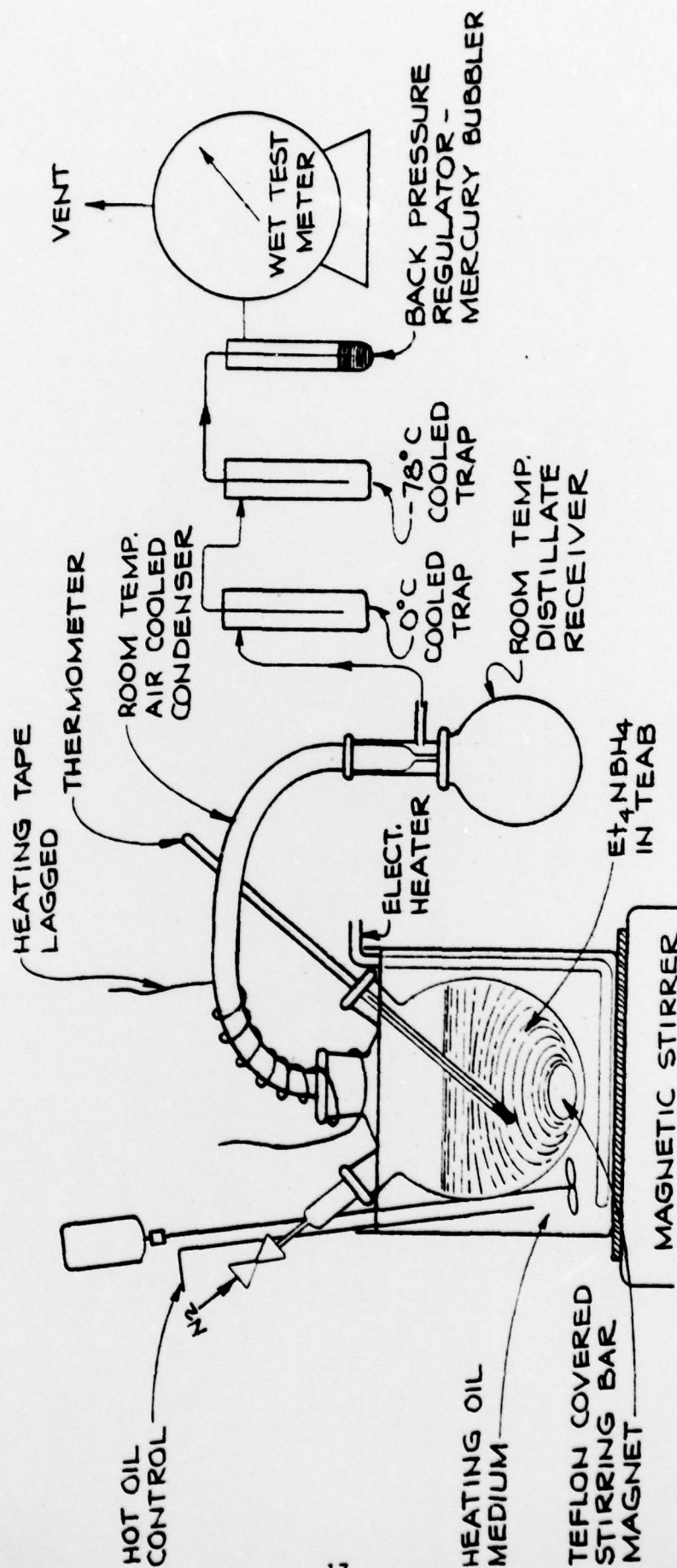


FIGURE III
SINGLE PLATE DISTILLATION REACTOR

Run 22 short duration high temperature reaction, produced predominately $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$, but in very low overall total yield. However the higher 190°C temperature did not adversely effect the $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ synthesis, based on in-house infrared analysis. N.M.R. conformation was not requested because of the small amount of product produced during the 35 minute run.

Thermolysis temperatures near 180°C appeared optimum in the single plate distillation reactor. Shorter reaction times at this temperature with lower concentrations of triethylamine borane produced the maximum yield of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ and minimum amount of $\text{B}_{12}\text{H}_{12}^{2-}$ derivative. The improved yields for runs 27, 28 and 29 were mainly attributed to the time-temperature relationship.

Evaluation of the heat transfer requirements with respect to the ratio of triethylamine borane to Et_4NBH_4 , at the above conditions, was further investigated at this point. The amount of triethylamine borane was reduced stepwise in Runs 28, 29, 31 and 33.

The maximum yield of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ was obtained in Run 31 where the triethylamine borane was reduced to 50% of the weight of Et_4NBH_4 . This amount of solvent just wets the solid starting material providing heat transfer benefits, but is not stirrable initially. It required 75 minutes of heat up time for the reactor mass to reach the desired 180°C temperature range, although off gasing starts below 100°C . Physical changes occur as the thermolysis proceeds. First a wet bubbling mass, developing at 75 minutes, slowly thins out to a readily stirrable slurry at 105-120 minutes. A longer reaction time was required, as less heat transfer solvent was used, to release an equivalent amount of triethylamine, H_2 and C_2H_6 (2.5 hours compared to 1.5 hours).

Using much less triethylamine borane as in Run 33, only 5 g heat transfer-solvent, 10% of the weight of starting Et_4NBH_4 , was not successful in promoting conversion under similar reaction conditions. Product recovered after 3.5 hours of thermolysis at 180°C contained a large amount Et_4NBH_4 according to in-house infrared and iodometric titration analyses.

A repeat of the potentially optimized run conditions of Run 31 was successfully carried out in Run 34. $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ yields, according to in-house infrared, suggested yields substantially above the 60% range. N.M.R. and L.C. analyses confirm these conditions with yields in the 36 to 56% range.

The presence of stainless steel in a finely divided form has been reported by Dr. Hill, et.al., to be advantageous in synthesizing $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ in the thermolysis of Et_4NBH_4 . Evaluation of stainless steel media present during thermolysis was made in a single test Run 30 with little obvious effect. Runs 29 and 30 were duplicates except for presence and absence of stainless steel catalyst. Stainless steel might be advantageous when Et_4NBH_4 is pyrolysed in the dry state. However scale-up problems using large amounts of dry powder Et_4NBH_4 and stainless steel media were considered more difficult than solvent thermolysis.

Thermolysis of Et_4NBH_4 in Mineral Oil - A non-boron based solvent, was accomplished in a single Run 35 with favorable results. Mineral oil was selected for desirable economic and engineering factors. Solubility of some intermediates in mineral oil during the thermolysis process may aid in $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ synthesis.

For comparison purposes the optimized reactor and reaction conditions of Run 31 and 34 were used to evaluate mineral oil as a potential heat transfer solvent. Heating at the same rate required 75 minutes for both solvent systems to reach the desired 180°C reaction temperature range. However mineral oil solvent required a longer reaction time for an equivalent off gas ratio. It required 8 hours of reaction to release near theoretical off gas, compared to 2.5 hours in Runs 31 and 34 using triethylamine borane solvent. The $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ content in the thermolysis product was reported to be appreciable according to in-house infrared analyses, N.M.R. based yield was 33.5% and L. C. based 47.3% on the solid product recovered.

CONCLUSIONS

At its present state of development, the expected yield of $(\text{Et}_4\text{N})_2\text{B}_{10}\text{H}_{10}$ from the Et_4NBH_4 thermolysis process is about 60%.

Optimized ratios of heat exchange solvent and starting Et_4NBH_4 presents a reactor stirring problem. Initially the reaction mixture is a slush not stirrable by usual laboratory methods. When heated to near 100°C it turns solid. As the reactant temperature is increased to near 180°C a liquid phase forms and stirring is possible.

Further successful scale-up of Et_4NBH_4 thermolysis will be dependent, to a large extent, on reactor geometry and variable speed stirring capability.

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